

# **ASSESSMENT OF CHROMIUM POLLUTION AT BAULA MINES, ORISSA**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF

**BACHELOR OF TECHNOLOGY  
IN  
MINING ENGINEERING**

**BY**

**BASANTA KUMAR KISHAN**

**10605010**



**Department of Mining Engineering**

**National Institute of Technology**

**Rourkela**

**2010**

# **ASSESSMENT OF CHROMIUM POLLUTION AT BAULA MINES, ORISSA**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

**BACHELOR OF TECHNOLOGY  
IN  
MINING ENGINEERING**

**BY**

**BASANTA KUMAR KISHAN**

**10605010**

**Under the Guidance of**

**Sk. Md. Equeenuddin**



**Department of Mining Engineering**

**National Institute of Technology**

**Rourkela**

**2010**



## **National Institute of Technology, Rourkela**

### **CERTIFICATE**

This is to certify that the thesis entitled “**ASSESSMENT OF CHROMIUM POLLUTION AT BAULA MINES, ORISSA**” submitted by **Sri Basanta Kumar Kishan** in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

**Date:**

**Sk. Md. Equeenuddin**  
**Assistant Professor**  
**Dept. of Mining Engineering**  
**National Institute of Technology**  
**Rourkela, Orissa-769008**

## **ACKNOWLEDGEMENT**

I wish to express my deep sense of gratitude and indebtedness to supervisor, **Sk. Md. Equeenuddin**, Department of Mining Engineering, N.I.T Rourkela for introducing the present topic and for his inspiring guidance, constructive criticism and valuable suggestion throughout this project work.

I am also thankful to other staffs in Department of Mining Engineering for providing all joyful environments in the laboratory and helping me out in different ways.

Last but not least, my sincere thanks to all our friends who have patiently extended all sorts of help for accomplishing this undertaking.

**DATE:**

**BASANTA KUMAR KISHAN**  
**Dept. of Mining Engineering**  
**National Institute of Technology**  
**Rourkela – 769008**

# CONTENTS

	Page
<b>Abstract.....</b>	<b>i</b>
<b>List of Figures.....</b>	<b>ii</b>
<b>List of Tables.....</b>	<b>iii</b>
<b>1. Introduction &amp; Objective</b>	<b>1</b>
1.1 Introduction.....	2
1.2 Objective.....	3
<b>2. Literature Review</b>	<b>4</b>
2.1 Chromium Chemistry.....	5
2.2 Natural Sources of Chromium.....	6
2.3 Pollution of water by Chromium.....	6
2.4 Harmful effect of Cr (VI) .....	8
2.5 Cr (VI) Retention by Mine overburden.....	8
2.6 Location and Geological set up of Nuasahi-Baula Complex.....	9
<b>3. Materials and Methods</b>	<b>11</b>
3.1 Sample Collection.....	12
3.2 Laboratory Work.....	12
3.3 Colorimetric Method.....	12
3.4 Desorption Experiment.....	13
3.5 Sequential Extraction of chromium.....	14
<b>4. Results and Discussions</b>	<b>15</b>
4.1 Mineralogy of Laterite Soil.....	16
4.2 Chromium in water.....	16
4.3 Desorption Experiment.....	17
4.4 Sequential Extraction of Chromium.....	19

<b>5. Conclusions.....</b>	<b>22</b>
<b>References.....</b>	<b>23</b>

# ABSTRACT

This study is conducted in and around one of the chromite mines of the Nuasahi-Baula igneous complex for assessing the Cr pollution. Hexavalent chromium was found between 0.002 and 0.006 ppm in groundwater and 0.008 to 0.036 ppm in mine discharges. The total chromium ranged between 0.002 and 0.007ppm in groundwater and 0.009 to 0.042 ppm in mine discharge water. The goethite rich overburden material at chromite mines is an efficient sink for the chromate anion. Leaching experiments using a saline solution, phosphate solution and tap water showed that phosphate solution release more hexavalent chromium compared to other two solutions. These results can be useful in evaluating natural attenuation of fertilizer-derived pollutants in the agricultural land near chromite mines. From the mineralogy it was found that the laterite contains more goethite mineral compared to other minerals. The concentration of chromium is more in laterite than overburden and soil. The impacts of chromium on the environment depend on the percentage of chromium in exchangeable fraction. The study shows that percentage of chromium is less in exchangeable fraction and more in residual fraction in in the study area. So the Cr bioavailability is low and toxicity is less.

## LIST OF FIGURES

FIG. NO.	TITLE	PAGE NO.
2.1	Eh-pH diagram of chromium	5
3.1	Calibration curve for Cr (VI)	13
3.2	Scheme of the selective sequential extraction	14
4.1	XRD pattern of laterite sample	16
4.2	Development of laterite cover at the chromite mines	17
4.3	Desorption of Cr (VI) in saline, phosphate solution and tap water at various period	18
4.4	Total concentration of Cr in laterite cover, soil and overburden(OB)	19
4.5	Distribution of Cr into various components	20



## LIST OF TABLES

TABLE NO.	TITLE	PAGE NO.
2.1	pH values at zero point of charge for HFO minerals	9
2.2	Stratigraphy of Baula-Nuasahi igneous complex	10
4.1	Dissolved chromium and pH in mine and ground water	17
4.2	Desorption of Cr (VI) from laterite soil into saline, phosphate solution and water	18
4.3	Percentage of Cr leached in different fractions	20

# CHAPTER 1

---

## *INTRODUCTION & OBJECTIVE*

## 1.1 INTRODUCTION

Chromium is a member of the transition metals, in group 6. Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm. Chromium exhibits a wide range of oxidation states. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable. From them +6 oxidation state is mobile in water and carcinogenic in nature. The locked up chromium in chromites that carry the major portion of the lithogenic Cr and the refractoriness of the mineral is an environmental blessing. If each of the Cr (III) atoms took up only one more atom of oxygen for conversion to a higher valance state, the entire atmospheric oxygen could be stripped out. However, before the earth attains such an anoxic disaster, life will be poisoned by Cr (VI) toxicity (Bartlett and James, 1986) as a result of Cr (III) to Cr (VI) conversion. Hexavalent Cr is known to be 100–1000 times more toxic than the trivalent form (Gauglhofer and Bianchi, 1991). In the hexavalent state, chromium exists as oxospecies such as  $\text{CrO}_3$  and  $\text{CrO}_4^{2-}$  that are strongly oxidizing. Hexavalent chromium may exist in aquatic media as water soluble complex anions and may persist in water. Hexavalent chromium is a strong oxidizing agent and may react with organic matter or other reducing agents to form trivalent chromium. The trivalent chromium will eventually be precipitated as  $\text{Cr}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ . Therefore, in surface water rich in organic content, hexavalent chromium will exhibit a much shorter life time. Any hexavalent chromium in soil is expected to be reduced to trivalent chromium which is lost from soil by aerial transport through aerosol formation and surface water transport through run off ([www.epa.gov/iris/toxreviews/0144tr.pdf](http://www.epa.gov/iris/toxreviews/0144tr.pdf)).

There has been an increasing demand for chromite ores in recent years. In the opencast mining processes, the chromite ore as well as waste rock material are dumped in the open ground without considering the environmental aspects and resulting in the oxidation of Cr (III) to Cr (VI). The result has been damage to the topography and leaching of chromium and other impurities to the groundwater as well as surface water bodies (Tiwary et al., 2005). Therefore, contamination of groundwater and soil in the vicinity of mines is expected.

## **1.2 OBJECTIVE**

This thesis has the following objectives

- Concentration of Cr in mine discharges and ground water
- Mineralogy of the soil
- Desorption of the Cr (VI) from the lateritic soil
- Sequential extraction of the Cr

# CHAPTER 2

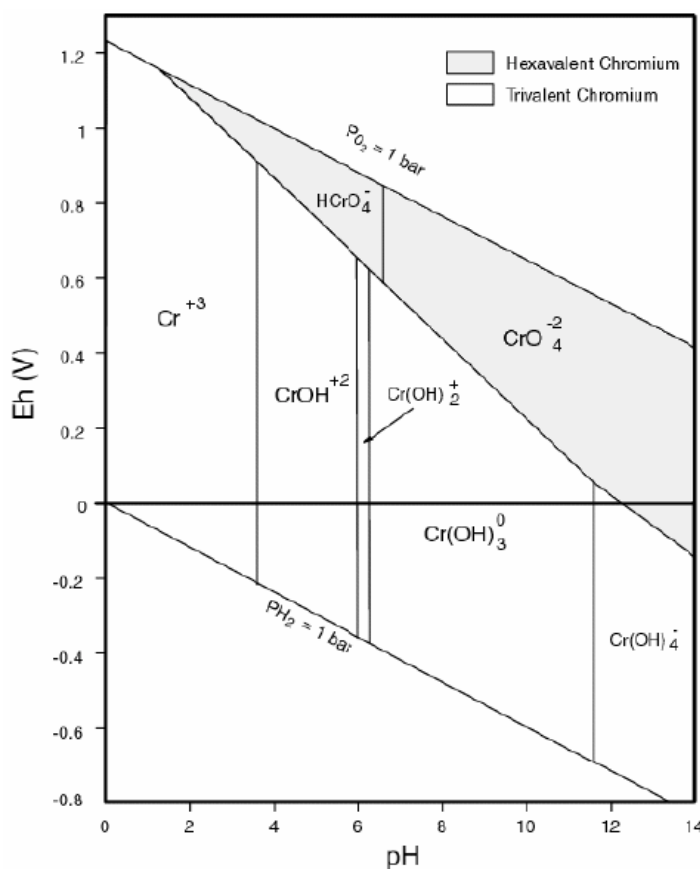
---

## ***LITERATURE REVIEW***

*CHROMIUM CHEMISTRY*  
*NATURAL SOURCES OF CHROMIUM*  
*POLLUTION OF WATER BY CHROMIUM*  
*HARMFUL EFFECT OF Cr (VI)*  
*Cr (VI) RETENTION BY MINE OVERBURDEN*  
*LOCATION AND GEOLOGICAL SET UP OF NUASAH-BAULA*  
*COMPLEX*

## 2.1 CHROMIUM CHEMISTRY

Chromium has a unique geochemical behaviour in natural water systems. Under strong oxidizing conditions, chromium is present in the Cr (VI) state and persists in anionic form as chromate. Cr (III) is the most common form of naturally occurring chromium, but is largely immobile in the environment. Redox potential Eh-pH diagrams present equilibrium data and indicate the oxidation states and chemical forms of the chemical substances which exist within specified Eh and pH ranges.



**Figure 2.1: Eh-pH diagram for Chromium**

(Sources: <http://www.epa.gov/nrmrl/pubs/625r00005/625r00005.pdf>)

The Figure 2.1 implies that the boundary separating one species from another is distinct; the transformation is so clear cut. Concentration, pressure, temperature, and the absence or presence of other aqueous ions can all affect which chromium species will exist. A measure of caution must be exercised when using this diagram as site-specific conditions can significantly alter actual Eh-pH boundaries. Under reducing conditions, Cr (III) is the most thermodynamically stable oxidation state. However, Cr (VI) can remain stable for significant

periods of time. Cr (III) exists in wide Eh and pH ranges. Cr (III) predominates as ionic (i.e.,  $\text{Cr}^{+3}$ ) at pH values less than 3.0. At pH values above 3.5, hydrolysis of Cr (III) in a Cr (III)-water system yields trivalent chromium hydroxy species [ $\text{CrOH}^{+2}$ ,  $\text{Cr(OH)}_2^+$ ,  $\text{Cr(OH)}_3$ , and  $\text{Cr(OH)}_4^-$ ] is the only solid species, existing as an amorphous precipitate.

## **2.2 NATURAL SOURCES OF CHROMIUM**

Chromium is one of the earliest elements to be immobilized in solids by crystallization during differentiation of magma. Therefore it is normally concentrated in the ultramafic and ultrabasic rocks. Dunite, peridotite, pyroxenite, and serpentine contain Cr at levels of 2400 ppm (Matzat and Shiraki, 1974). The distribution of total Cr in natural groundwaters was investigated by Barnes and Langmuir (1978). They found total Cr thresholds, corresponding to the 97.7 percentile, of 10–19ppb for 647 groundwaters associated with carbonate rocks, sandstones (including quartzites, arkoses, grey wacks, and conglomerates), shales (comprising clays, siltstones, and slates), and felsic to intermediate igneous and meta-igneous rocks. By contrast, a total Cr above the threshold was found for 35 groundwaters coming from mafic and ultramafic igneous and meta –igneous rocks. In fact the worldwide average Cr contents of peridotites and basalts (1800 and 185ppm, respectively) are much higher than those of limestones (11 ppm), granites (22 ppm), sandstones (35 ppm), and shales (90 ppm; (Faure, 1992). However these data are insufficient to define the natural (background) concentrations of Cr (VI) and Cr (III) in waters, a facet of utmost importance due to their different toxicity. Concentrations of Cr (VI) reaching 12 ppb and Cr (III) 11 ppb were recently found in groundwaters interacting with ultramafic rocks (Robles-Camacho and Armienta, 2000), indicating that these lithotypes may cause natural pollution of waters in not only Cr (III) but also Cr (VI).

## **2.3 POLLUTION OF WATER BY CHROMIUM**

Water pollution has been a serious threat to mankind since last few decades. The common polluting sources are domestic sewage, mine drainage, and industrial effluents. Natural weathering of rocks, which supplies a significant amount of toxic elements and compounds to surface as well as ground water acts as a background to the pollution effect. Metal pollution

of water by different sources has been studied by several workers. Chromium contamination from Sukinda chromite mine, leading to the pollution of river and groundwater has been reported by Godgul and Sahu (1995). Chromium pollution is caused mainly due to weathering of mafic or ultramafic rocks (Fantoni et al., 2002) and industrial waste (Singh et al., 2009).

In nature, the dispersion of pollutants is partly controlled by clay minerals, metal oxides and organic matter which acts as sinks for pollutants (Raymahashay, 1996). The surface charge of clay minerals is pH dependent. At pH below the zero point charge (ZPC), the surface is positively while the charge becomes negative at higher pH. As a result, anion exchange is more prominent at low pH whereas cation exchange capacity increases with increasing pH. Adsorption of positively charged metal ions on clay surfaces has been widely observed. The clay minerals which occur in soil profiles as well as stream sediments remove the pollutants when water containing toxic metals pass through them. Metal oxides and hydroxides like those of Al, Fe and Mn also act as scavengers of trace elements. The surface of the hydrous oxides has a positive charge at pH below ZPC and negatively charge at pH value. This enables them to adsorb the toxic elements in high as well, as low pH conditions. Lateritic soil and organic matter similarly remove ionic pollutants from waste water.

The geochemical cycle of Cr may also involve reduction of Cr (VI) to Cr (III) in the presence of ferrous ( $\text{Fe}^{2+}$ ) iron and organic matter (Richard and Bourg, 1991) (Sedlak and Chan, 1997). This principle has been utilized to treat Cr (VI) – rich mine drainage with  $\text{FeSO}_4$  which results in the precipitation of  $\text{Cr}(\text{OH})_3$ . Moreover, biologically mediated Cr (VI) reduction in the presence of soil bacteria has been recommended as a method of Cr-removal (Ligy Philip, 1997). This process may be active in the top soil zone around chromite mines.

In Sukinda area, the lateralization process involving oxidation and alternation of the serpentines creates alkaline pore water which facilitates the generation of Cr (VI) from the inert chromites and causes hazardous chromium pollution of water. Godgul and Sahu (1995) have found Cr (VI) in some quarry waters from Sukinda chromite field, above the permissible limit recommended by world health organization. The enhanced Cr levels of mine floor water samples in Sukinda according to them, are suggestive of the release of immobile Cr (III) after oxidation either from chromite or silicate and the likely movement of the oxidised species to the groundwater. The steady release of Cr from Sukinda into the Damsala river has been enhanced the Cr levels in the sediments and water of the Brahmani



river estuary near Dharma region of Bay of Bengal. So, while Cr (III) either in ultramafic rocks or in chromite deposits is rarely a danger to the environment, altered and oxidised chromite may pose a threat to the environment by dispersing significant quantity of Cr (VI) to the aqueous system. But this pollution effect is partly neutralized in nature by the presence of goethite in lateritic rocks present chromite mines. This is because goethite, a hydrated iron-oxide, carries a positive charge on its surface in its colloidal state, thereby adsorbing the negatively charged  $\text{CrO}_4^{2-}$  from the ground water during its percolation through the rocks.

## **2.4 HARMFUL EFFECT OF Cr (VI)**

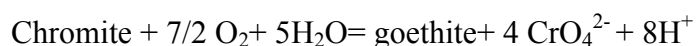
Chromium (VI) is one of the most toxic water pollutant and is comparatively more toxic than trivalent compounds. Chromium and its compounds are known to cause cancer of the lungs, nasal cavity and paranasal sinus and is suspected of causing cancer of the stomach and larynx. Hexavalent chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. Trivalent chromium, which is the more common variety of chromium compounds, is not transported into cells. Cr (III) is considered to be essential to mammals for the maintenance of glucose, lipid and protein metabolism. Chromium can act directly at the site of contact or be absorbed into, or through, human tissue. Chromium (VI) can act as an oxidant directly on the skin surface or it can be absorbed through the skin, especially if the skin surface is damaged. Chromium absorbed into the blood does not accumulate in any organs at significant concentrations. In metabolism studies, injected and ingested chromium was found mainly in the liver, kidneys, and blood. Breathing in high levels of Cr (VI) ( $>2 \mu\text{g}/\text{m}^3$ ) containing dust particles in the form of compounds like chromic acid or chromium tri-oxide, can cause irritation to the respiratory system. The permissible limit of Cr (VI) in drinking water is  $50 \mu\text{g}/\text{L}$  and total Cr is  $100 \mu\text{g}/\text{L}$  ([www.epa.gov/iris/toxreviews/0144tr.pdf](http://www.epa.gov/iris/toxreviews/0144tr.pdf)).

## **2.5 RETENTION OF Cr (VI) BY MINE OVERBURDEN**

Chromium is mined as its oxide ore chromite  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ . Some of the largest opencast mines of India occur in the state of Orissa. Generally the chromite ore occurs in the form of discontinuous bands and lenses and confined to the altered dunite-peridotite, serpentine has been extensively weathered by atmospheric and percolating ground water. The  $\text{FeO}$

component of primary minerals like chromite, olivine and serpentine has been oxidized to group of Fe (III) like goethite,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and maghemite,  $\gamma\text{-Fe}_2\text{O}_3$ . These are the main constituents of the thick laterite-limonite overburden over the ore body. It is apparent that under the same oxidizing condition Cr (III) in chromite is mobilised into ground water as the hexavalent  $\text{CrO}_4^{2-}$  ion.

The overall process can be represented by a reaction of the type:



The situation is favourable for quantitative adsorption of the Cr (VI) anion on the positively charged surface of goethite. The goethite is positively charged as the pH of water is below the ZPC (Zero Point Charge) value of goethite. At ZPC the net charge on the mineral is zero (Raymahashay, 1998). For individual minerals, different authors have cited a variety of values as shown in Table 2.1.

**TABLE 2.1: pH values at Zero point of charge for HFO minerals (Equeenuddin et al., 2008)**

Minerals	pH at ZPC
Magnetite, $\text{Fe}_3\text{O}_4$	6.5
Hematite, $\text{Fe}_2\text{O}_3$	5 to 9
Goethite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	6 to 7
	7.3 to 7.8
	9.5
Maghemite, $\gamma\text{-Fe}_2\text{O}_3$	6.7
Amorphous $\text{Fe}(\text{OH})_3$	8.5

## 2.6 LOCATION AND GEOLOGICAL SET UP OF BAULA-NUASAHU COMPLEX

Deposits of chromite in Baula-Nuasahi area of Kendujhar district was discovered in 1942 and mining started from 1943. The area around Nuasahi ( $21^\circ 17' \text{ N}$ ;  $86^\circ 20' \text{ E}$ ) lies at the south eastern fringe of Baula state forest and is connected to S.E railway and N.H.5 at Bhadrak town by an all weather 45 kilometers long metal road passing through Bidyadharpur barrage and Agarpara. The important features of the area include a dam on Salandi river and a

barrage at Bidydharpur. In Boula-Nuasahi sector, three mines are in active operation. Here, chromite is mostly lumpy and the wall rock is hard serpentine. Orissa Mining Corporation Limited (OMCL), a State Government undertaking is engaged in mining and processing of chromite ore in Keonjhar district of Orissa. Bangur Chromite mining lease of OMCL is located in Anandpur subdivision of Keonjhar district in Orissa. The total geological reserve of chromite ore in the lease-hold has been estimated to be 2.75 million tonnes (Mt).

The area around Boula-Nuasahi consists of older quartzites which include massive, ferruginous and micaceous varieties. The ultramafic body to the west of village Nuasahi extends for 3 kilometres in a NNW-SSE direction. This is a dyke like steeply incline body having distinct intrusive relationship with the older quartzites and epidiorite hills to the north. The ultramafic body has a maximum width about 1 kilometre in the middle tapering gradually towards north and south and mainly consists of serpentinitised dunite-pridotite core and a subordinate amount of pyroxenite, almost in a bysmalith form. The Stratigraphy of Boula-Nuasahin igneous complex (Sahoo, 1963) is given in Table 2.2

**Table 2.2: Stratigraphy of Baula-Nuasahi igneous complex**

Recent to Pleistocene		Soil, Alluvium, Laterite
<hr/>		
Unconformity		
		Dolerite dykes
		Granite
Precambrian	Ultramafics	Granophyre
		Gabbro-anorthosite with Ti-V magnetite
		Ore bodies Enstalite-Peridotite and dunite
		With chrome ore
	Meta sediments and metavolcanics	Quartzite, quartz-mica schist, quartz-sericite schist
<hr/>		
Base not seen		

# CHAPTER 3

---

## *MATERIALS AND METHODS*

### **3.1 SAMPLE COLLECTION**

Mine discharges, ground water, soil and overburden were collected from the Nuasahi Boula chromite mines area in the month of December, 2009. Mine discharges were collected from the OMC quarry; ground water from the near by village; overburden from OMC dump site, and soil and laterite cover from the surroundings.

Soil and overburden samples were collected in the air tight polythene packet. Water samples were collected in the acid rinsed polyethylene bottles in duplicates. Non-filtrate part was used for measuring pH and Cr (VI) while filtrate part was acidified with  $\text{HNO}_3$  to bring pH less than 2. The acidify part was used for the analysis of total Cr.

### **3.2 LABORATORY WORK**

Soil and overburden samples were powdered and sieved through (63  $\mu\text{m}$ ) for subsequent analysis.

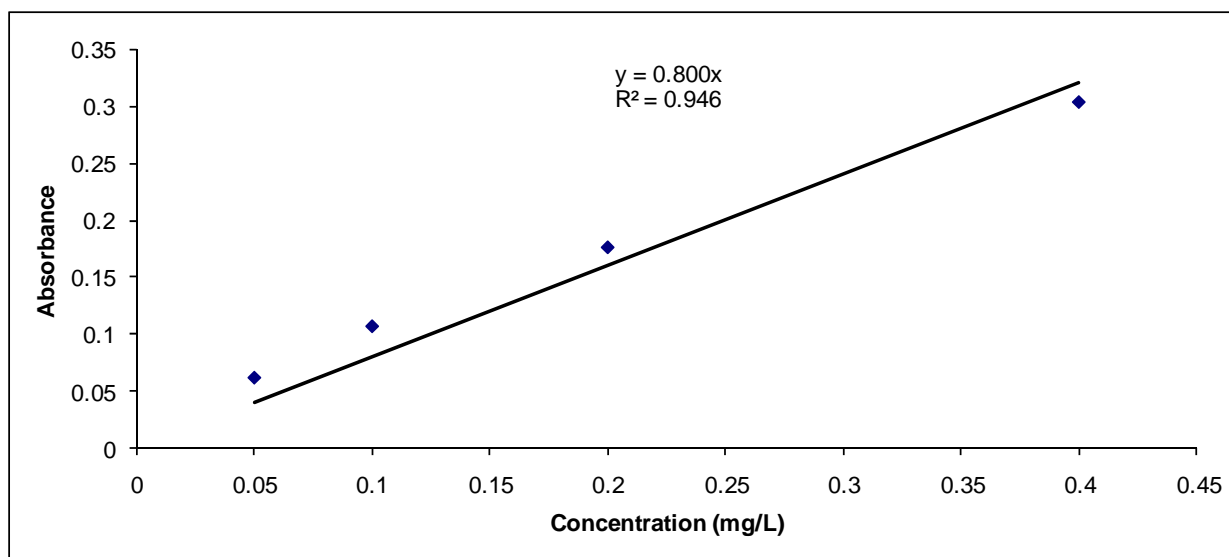
Mineralogy of soil and overburden was studied using a Phillips PW-1710 X-ray diffractometer (XRD) employing  $\text{CuK}\alpha$  radiation at 1.2°/minute scanning rate. Total concentration of Cr in soil and overburden was determined using Philips PW 2400 X-ray fluorescence from the press pellets.

Total Cr in mine discharges and ground water samples were analyzed using Atomic Absorption Spectrophotometer (PerkinElmer Analyst300). Hexavalent Cr was analyzed using the colorimetric method following Standard Methods (1985).

### **3.3 COLORIMETRIC METHOD**

Stock solution of 1000 ppm Cr (VI) was prepared by dissolving 2.8 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1000ml water. By diluting the stock solution, standard solutions of 0.05 ppm, 0.1 ppm, 0.2 ppm, and 0.4 ppm Cr (VI) was prepared for calibration purpose.

100 ml of solution was taken. 0.2 N  $\text{H}_2\text{SO}_4$  was added to the solution and then, 2 ml of diphenylcarbazide solution was added and mixed thoroughly. The solution was kept for 5 to 10 minute. A red violet colour was developed. The absorbance at 540 nm wavelength was measured by spectrophotometer (EI-1305). A calibration curve was constructed by plotting absorbance value against concentration (Figure 3.1).



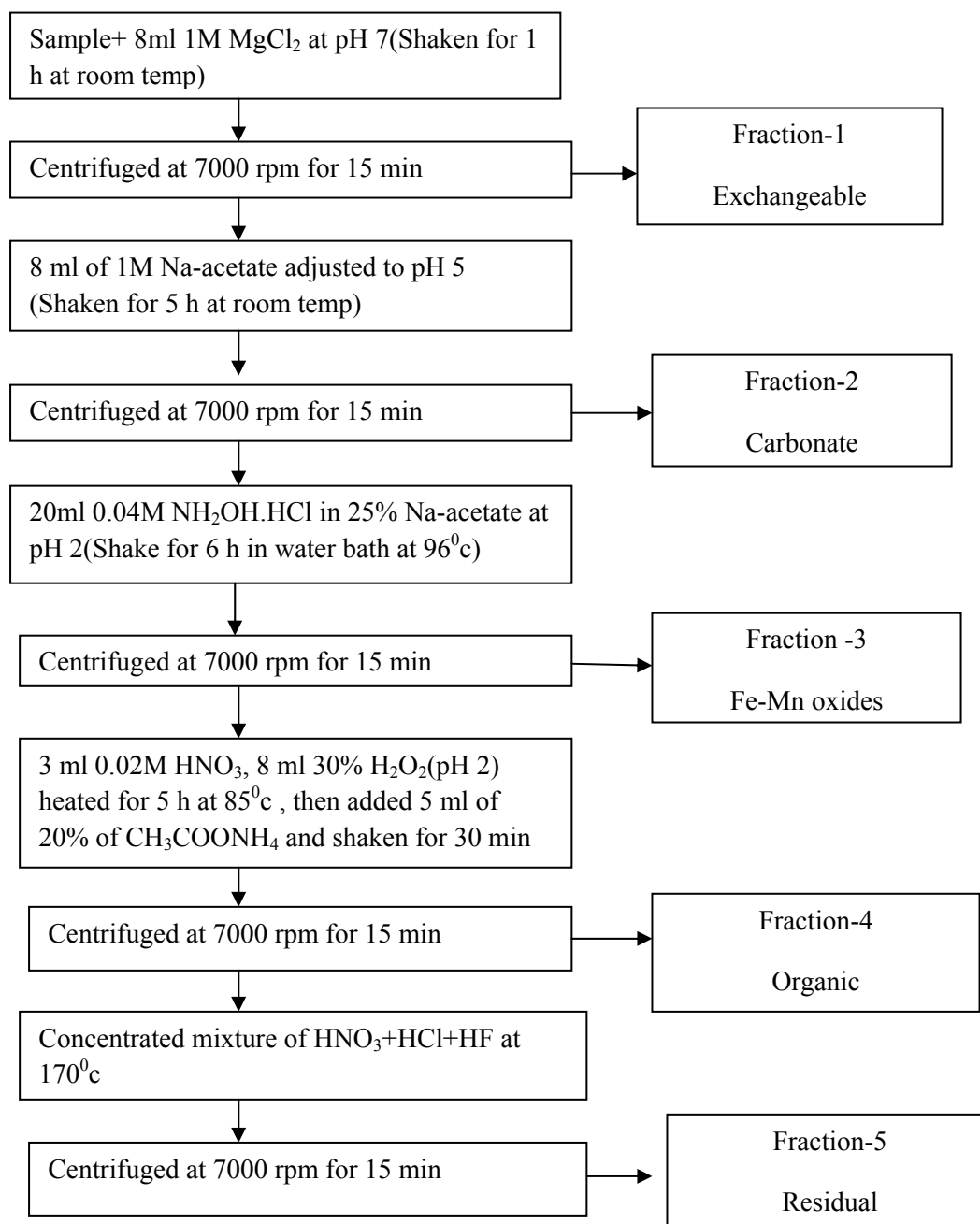
**Figure 3.1 Calibration curve for Cr (VI)**

### **3.4 DESORPTION EXPERIMENT**

Cr (VI) was leached out from laterite soils into 1) a saline solution, 2) Phosphate solution 3) tap water. The samples were powdered and sieved between 230 and 200 mesh (0.065 to 0.074 mm) size. For desorption into saline solution, 1 g of sieved sample was stirred into 100 ml distilled water containing 1.74 gm NaCl and 0.05 gm  $\text{NaHCO}_3$ . This solution has pH 8 (Bisoi, 1990). After a contact period of 24 hours, the suspension was filtered through whatman 42 paper and Cr (VI) was determined in the clear solution by colorimetric method as outlined above. For desorption into phosphate solution, 1gm of sieved sample was stirred in 0.1M  $\text{PO}_4$  solution prepared from  $\text{KH}_2\text{PO}_4$ .

### 3.5 SEQUENTIAL EXTRACTION OF CHROMIUM

An attempt was made to estimate the percentage of chromium associated with different fractions such as exchangeable, organic, Fe-Mn oxide, carbonate and residual fractions by sequential extraction procedure (SEP) (Figure 3.2).



**Figure 3.2: Scheme of the selective sequential extraction (Tessier et al., 1979)**

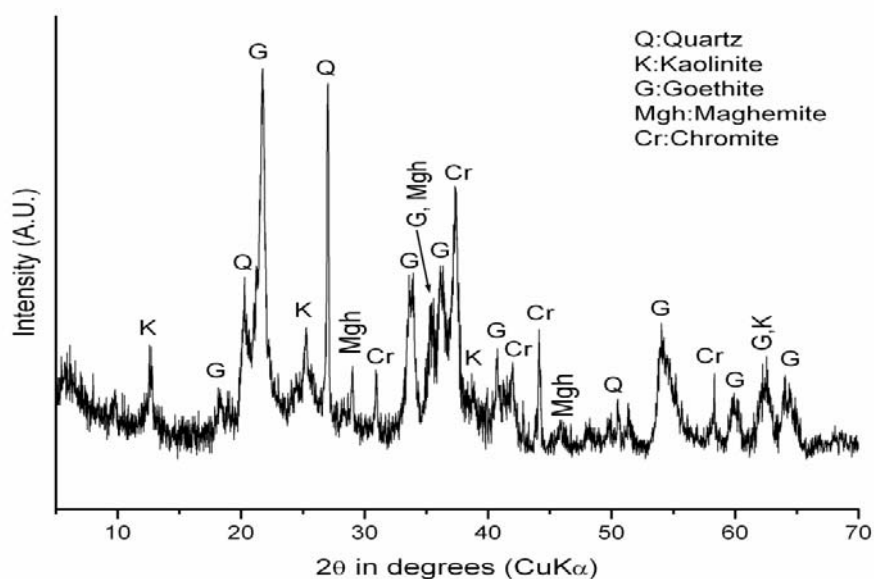
# CHAPTER 4

---

## *RESULTS AND DISCUSSIONS*



## 4.1 MINERALOGY OF LATERITE SOIL



**Figure-4.1: XRD pattern of laterite sample.**

X-ray diffraction pattern of the laterite soil is shown in Figure 4.1. It is observed that laterite is mainly composed of quartz, goethite, kaolinite and chromite with trace amount of mahgemite.

## 4.2 CHROMIUM IN WATER

Concentrations of Cr in various water bodies are given in Table 4.1. The pH of mine discharges ranges between 7.6 and 7.9 which is higher than the pH of ground water whose pH ranges between 6.7 and 7.2. Concentration Cr in mine and ground water ranges from 0.009 to 0.042 ppm and less than 0.001 to 0.007 ppm respectively. From the Table 4.1, it can be confirmed that most of the Cr occurs in the form of Cr (VI) due to very less difference in their respective concentration in both mine and ground water. The amount of Cr and Cr (VI) is below permissible limit in both type of water. The concentration of both total Cr and Cr (VI) in mine water is much higher than groundwater. This sharp decrease of the Cr concentration in ground water in comparison to mine water is apparently due to the retention of Cr (VI) in the form of  $\text{CrO}_4^{3-}$  anion onto the positively charged surface of laterite which is mainly composed of goethite. Lateritic cover is very extensive in the mining area as shown in Figure 4.2. The adsorption occurs during percolation of groundwater through the lateritic soil

cover. Similar kind of observation was earlier reported in near by Sukinda chromite mines (Raymahashay et al., 1998).

**TABLE 4.1: Dissolved chromium and pH in mine and ground water**

Sample	pH	Cr (VI) (ppm)	Total Cr (ppm)
Mine Discharge water	7.7	0.011	0.013
	7.6	0.014	0.015
	7.9	0.036	0.042
	7.8	0.008	0.009
Ground water	7.5	Nil	Nil
	6.7	Nil	Nil
	6.7	0.002	0.002
	7.2	0.006	0.007



**Figure 4.2: Development of laterite cover at the chromite mines**

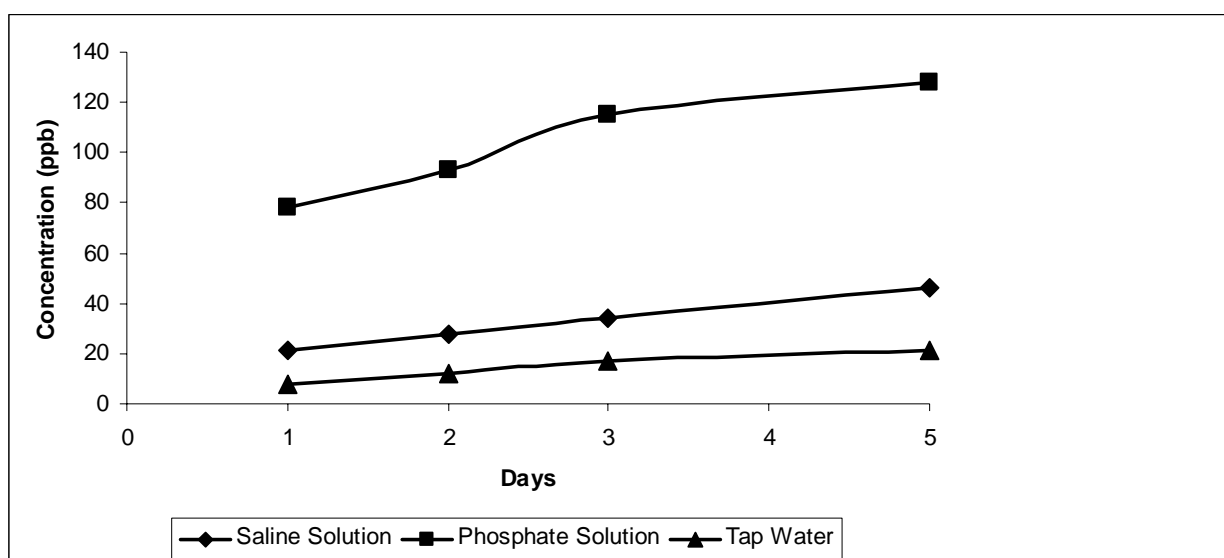
### 4.3 DESORPTION EXPERIMENT

In order to estimate the amount Cr (VI) adsorbed in laterite soil, non-destructive desorption experiment was carried out. The concentration of Cr (VI) released after desorption using three different solution, namely, saline solution, phosphate solution and normal tap water is shown in Table 4.2 and Figure 4.3. It is observed that release of Cr (VI) increases with increase in contact time. Phosphate solution released maximum Cr (VI) followed by saline

solution and tap water. This is possibly due to the similar specific adsorption mechanisms for both chromate and phosphate (Bartlett and James, 1988). Fendorf et al. (1997) showed that  $\text{CrO}_4^{2-}$  form an inner sphere complex at the goethite-water interface. Hsia et al. (1993) also confirmed the inner sphere adsorption of chromate onto iron hydroxide. Chromate adsorption onto clay was suppressed in the presence of phosphate (Aide and Cummings, 1997). In the saline condition, like at the mixing zone with sea, increase in salinity causes desorption of metals and suppress the adsorption process (Maest et al., 1990). Mayer and Schick (1981) reported the removal of chromate is ineffective under very high salinity regime by the estuarine sediments.

**TABLE 4.2: Desorption of Cr (VI) from laterite soil into saline, phosphate solution and water**

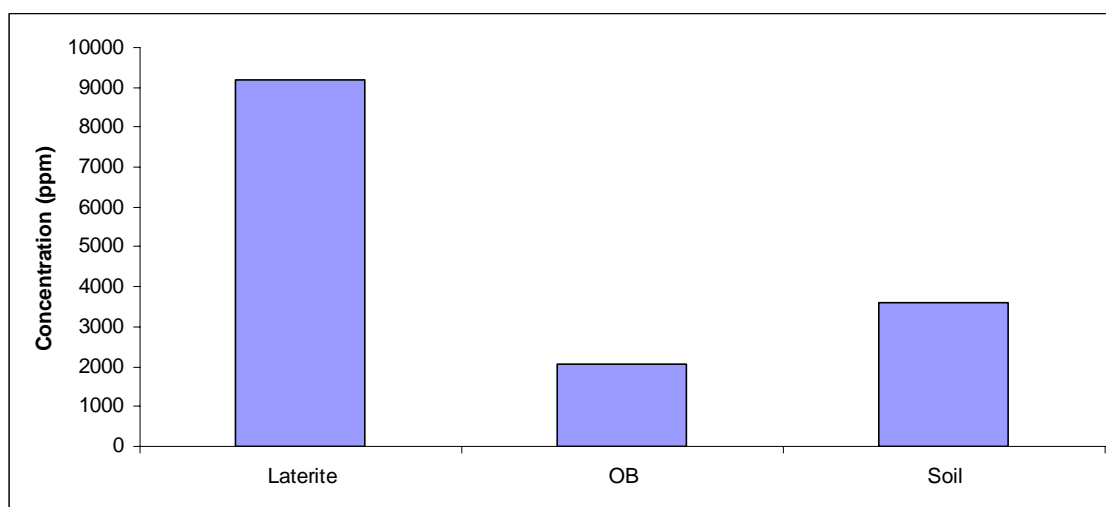
Day	Saline Solution(ppb)	Phosphate Solution(ppb)	Tap water(ppb)
1	21	78	8
2	28	93	12
3	34	115	17
5	46	128	21



**Figure-4.3: Desorption of Cr (VI) in saline, phosphate solution and tap water at various period**

#### 4.4 SEQUENTIAL EXTRACTION OF CHROMIUM

The concentration of Cr in soil, overburden and laterite cover provides just partial information of its potential impact. However, its association with various fractions is useful to assess the potential environmental and human health impact through mobilization. The metals mainly occur in soil, overburden and laterite through five major mechanisms, exchangeable (Exch), with organic matter (Org), with carbonates (Carb), with Fe-Mn oxides and hydroxides (Fe-Mn), and residual (Res). Metals in exchangeable fraction considered to be most mobile and readily available for biological uptake in environment (Gadde and Laitinen, 1974). The organic fraction represents metals held by complexation, adsorption, and chelation process. Under oxidising condition it release metals bound to those materials. Metals bound to Fe-Mn oxides and hydroxides fraction are unstable under reducing conditions. Metals bound to carbonates are sensitive to pH changes with the lowering of pH being associated with the release of metal cations. The residual fraction contains naturally occurring minerals which may hold trace metals within their crystal lattices and unlikely to be released from the soil and sediments thus it is considered to be chemically most stable and immobilized. Thus the bioavailability is low and toxicity is less.



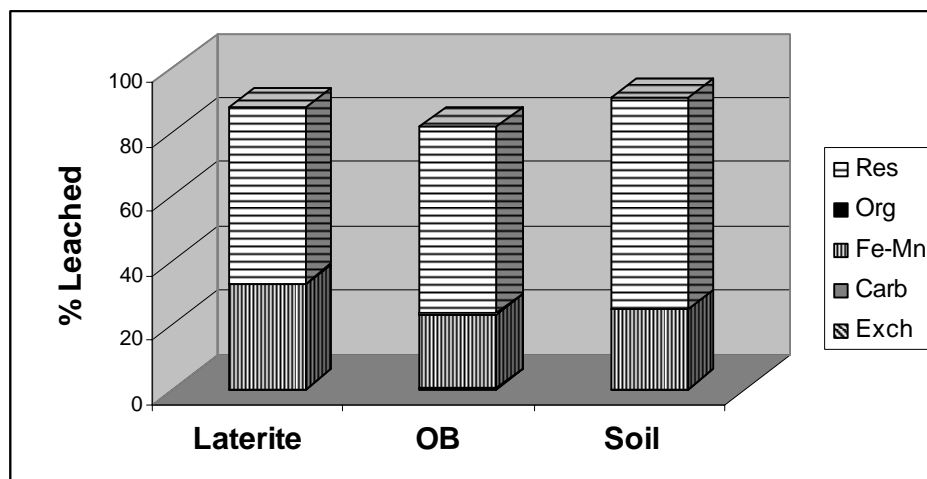
**Figure 4.4.: Total concentration of Cr in laterite cover, soil and overburden (OB)**

Total Cr concentration in the study area in soil, overburden and laterite cover is given in Figure 4.4. It is observed that the concentration of Cr in laterite cover is much higher than overburden and soil. This is due to the presence of goethite in laterite. The concentration of chromium is also much higher than its crustal abundance, which is 126 ppm.

**TABLE 4.3: Percentage of Cr leached in different fractions**

	% leached				
Sample	Exchangeable	Carbonate	Fe-Mn	Organic	Residual
Laterite	0.03	0.13	32.17	0.13	54.65
OB	0.15	0.11	23.09	0.14	58.11
Soil	0.09	0.06	24.55	0.08	66.03

Fractionation result of Cr is given in Table 4.3 and Figure 4.5. Fractionation result indicates that Cr is mostly associated in residual fraction followed by Fe-Mn bound and carbonate and/or organic and exchangeable. So the over all chromium toxicity is less in Baula mines. However, if the area would change into the reduce condition in future then the Fe-Mn bound Cr is likely to release into solution and can pose severe Cr pollution.



**Figure: 4.5: Distribution of Cr in various components**

# CHAPTER 5

---

## *CONCLUSIONS*

## 5. CONCLUSIONS

Based on the foregoing results and discussions, it can be concluded that hexavalent chromium was ranged between 0.002 and 0.006 ppm in groundwater and 0.008 to 0.036 ppm in mine discharges which are below the permissible limit. The total chromium ranged between 0.002 and 0.007 ppm in groundwater and 0.009 to 0.042 ppm in mine discharge water. This decrease in the concentration of Cr is apparently might be due to the retention of  $\text{CrO}_4^{3-}$  anion on the positively charged surface of goethite during percolation of ground water through the lateritic cover soil. Goethite was found to be one of the major components of the lateritic soil in addition to quartz, kaolinite and chromite with trace amount of mahgemite. Desorption experiments indicates that Cr (VI) are well retained in the laterite soil and maxium Cr (VI) was released into phosphate solution. The experiment results will be helpful in evaluating the fertilizer derived Cr (VI) in the study area. Total Cr in the soil and overburden is very high in comparison to its crustal abundant. Fraction study of Cr in soil and overburden indicates that bioavailability of Cr is less, and mostly associated with residual fraction.

## REFERENCES:

- Aide M.T. and Cummings M.F (1997), The influence of pH and phosphorus on the adsorption of chromium (VI) on boehmite. *Soil Science*, 162, pp 599–603.
- Barnes H.L. and Langmuir D (1978), *Geochemical prospecting hand-book for metals and associated elements*. National Science Foundation Grant no AER77-06511 AO2, Annual Report.
- Bartlett R.J. and James B.R (1988), Mobility and bioavailability of chromium in soils. In 'Chromium in the natural and human environments'. (Eds JO Niragu, E Nieboer) pp 267-303. (John Wiley and Sons Inc.: New York).
- Bisoi S.K (1990), Phosphate adsorption –desorption experiments with river clay minerals under upper estuary condition; Unpublished M.tech. thesis, I.I.T. Kanpur.
- Equeenuddin Sk.Md. and Raymahashay B.C (2008), Retention of Anionic pollutants by overburden material at chromite mines: An Experimental Investigation. *Asian Journal of water, Environment and pollution*, 5, pp 109-113.
- Fantoni D., Brozzo G., Canepa M., Cipolli F., Marini L., Ottonello G. and Zuccolini M.V (2002), Natural hexavalent chromium in groundwater interacting with ophiolitic rocks. *Environmental Geology*, 42, pp 871-882.
- Faure G (1992), *Principles and applications of inorganic geochemistry*. Maxwell-Macmillan, New York.
- Fendorf S., Eick M. J., Grossl P. and Sparks D.L (1997), Arsenate and chromate retention mechanisms on goethite .1. Surface structure. *Environmental science and technology*, 31, pp 315.
- Gadde R.R. and Laitinen H.A (1974), Studies of heavy metals absorption by hydrous Fe and Mn oxides. *Analytical Chemistry*, 46, pp 2022– 2226.
- Gaughhofer J. and Bianchi V (1991), Chromium. In: Merian E (Ed), *Metals and their compounds in the environment*. New York: VCH Publisher, pp 853-878.



- Godgul G. and Sahu K.C (1995), Chromium contamination from chromite mine. *Environmental Geology*, 25, pp 251-257.
- Hsia T.H., Lo S.L., Lin C.F. and Lee D.Y (1993), Chemical and spectroscopic evidence for specific adsorption of chromate on hydrous iron oxide. *Chemosphere*, 26, pp 1897-1904.
- Maest A. S., Crerar D. A., Stallard R.F. and Ryan J (1990), Metals and nutrient behaviour in the Raritan estuary, New Jersey, USA: the effect of multiple fresh water and industrial waste inputs. *Chemical Geology*, 81, pp 133-150.
- Matzat E. and Shiraki K (1974), Chromium. *Handbook of Geochemistry*, 11(3) :24(A).
- Mayer L. M. and Schick L. L (1981), Removal of hexavalent chromium from estuarine water by model substrates and natural sediments. *Environmental Science & Technology*, 15, pp 1482-1484.
- Philip L (1997), Studies on the potential mechanism and application of bacterial isolates from contaminated soils for heavy metal decontamination and biotransformation of Cr (VI) ; Unpublished Ph.D thesis, I.I.T. Kanpur.
- Raymahashay B.C (1996), *Geochemistry for Hydrologists*; Allied publishers Ltd., New Delhi.
- Raymahashay B.C. and Praharaj T (1998), Chromate uptake by lateritic soils: Similarly with phosphate. *Indian journal of Environmental protection*, 18, pp 933-936.
- Raymahashay B.C (1998), Metal uptake by geologic materials: Experiments and field applications. *Metals Materials and Processes*, 10, pp 379-386.
- Richard F.C. and Bourg C.M (1991), Aqueous Geochemistry of chromium: A Review. *Water Research*, 10, pp 824-827.
- Robles-Camacho j., Armienta M.A (2000), Natural chromium contamination of groundwater at Leon valley, Mexico. *Journal of Geochemical Exploration*, 68, pp 167-181.
- Sahoo R.K (1995), *Geology and Mineral Resources of Orissa*. Bhubaneswar, Society of Geoscientists and Allied Technologists.

- Sedlak D.L. and Chan P.G (1997), Reduction of hexavalent chromium by ferrous iron. *Geochimica et Cosmochimica Acta*, 61, pp 2185-2192.
- Singh R.K., Sengupta B., Bali R. and Shukla B.P (2009), Identification and Mapping of Chromium (VI) Plume Groundwater for Remediation: A Case Study at Kanpur, Uttar Pradesh. *Journal Geological Society of India*, 74, pp 49-57.
- Singh V.S., Dhakate R. and Hodlur G.K (2008), Impact of assessment of chromite mining on groundwater through simulation modelling study in chromite mining area, Orissa, india. *Journal of Hazardous Materials*, 160, pp 535-547.
- Standard Methods (1985). Standard methods for the examination of water and waste water. American Public Health Association, New York.
- Tessier A., Campbell P.G.C. and Bisson M (1979), Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51, pp 844-851.
- Tiwary R.K., Dhakate R., Ananda Rao.V. and Singh V.S (2005), Assessment and Prediction of contaminant migration in groundwater from chromite waste dump. *Environmental Geology*, 48, pp 420-429.
- <http://en.wikipedia.org/wiki/Chromium>
- <http://www.epa.gov/nrmrl/pubs/625r00005/625r00005.pdf>
- [www.epa.gov/iris/toxreviews/0144tr.pdf](http://www.epa.gov/iris/toxreviews/0144tr.pdf)